

Description

This invention concerns a new method for producing O-alkylamidothiophosphoric acid potassium salts starting from O,O-dialkylthiophosphoric acid ester amides.

Methods for producing O-alkylamidothiophosphoric acids salts from the corresponding amides are known from DE-OS 21 35 761, US Patent 36 70 057, and Houben-Weyl, Methods of Organic Chemistry [in German], Vol. XII/2, p. 754 (1964).

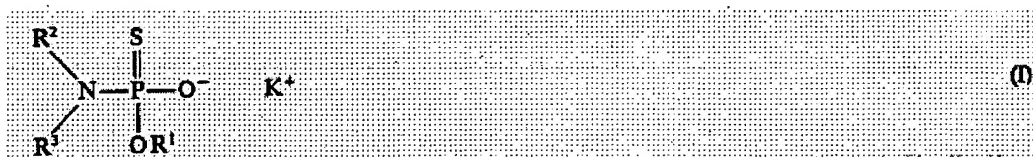
US Patent 36 70 057 describes the reaction of O,O-dialkylthiophosphoric ester N-alkylamides with alkali metal hydrosulfides in suitable solvents. This method, however, has the disadvantage that mercaptans are formed as a byproduct and, because of their toxicity and foul odor, they are technically difficult to manage. For this reason, a costly wastewater treatment is necessary.

Also, it is disclosed in this patent that if O,O-dialkylphosphoric ester amides with a non-alkylated amido group are used, dealkylation with alkali metal hydroxides in a solvent is possible. This statement, that only phosphoric acid ester amides having an unsubstituted amino group can be used in this method, is supported by Houben-Weyl, cited above. The possibility of decomposition of the products with elimination of ammonia is indicated there. Moreover, in this method the removal of the resulting alkali chloride from the reaction solution is difficult and involves high losses, since the alkali chloride has similar behavior in solution to the reaction product.

Dealkylation of N,N-dialkylthiophosphoric ester amides by means of dithiocarbamic acid salts is known from DE-OS 21 35 761. In this method, too, the processing of the products involves considerable expense, since the resulting dithiocarbamic acid esters have to be separated from the reaction mixture.

Surprisingly, it has now been found that N,N-dialkylthiophosphoric acid ester amides can be dealkylated in very good yield by means of potassium hydroxide at elevated temperature.

Therefore, the object of the invention is a method for producing O-alkylamidothiophosphate salts of formula (I)



in which

R¹ and R³ independently mean (C₁-C) alkyl and

R² means hydrogen or (C₁-C) alkyl,

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which is characterized by the fact that a compound of formula (II)



is reacted with potassium hydroxide at elevated temperature.

A (C₁-C₄) alkyl residue is preferably used as alkyl residue in the formulas given above. KOH is used in particular, in an approximately stoichiometric amount. The reaction progresses nearly quantitatively. If KOH is replaced by NaOH as reactant, the yields decrease drastically, since decomposition products are formed. For this reason, the fact that a quantitative reaction is observed with KOH is all the more surprising.

As reactants [sic], temperatures between 80°C and 150°C are chosen, depending on the residues R¹-R³. The resulting alcohol R¹OH distills out at these temperatures. The desired end product remains in the residue.

The method can be carried out without solvents or in the presence of water or of nonpolar organic solvents, i.e., aromatic solvents like toluene, xylene, chlorobenzene or even higher-boiling aliphatic hydrocarbons like octane, decane or hydrocarbon mixtures with boiling points between 110°C and 200°C. Preferably, the reaction is carried out in aromatic solvents, especially in xylene.

The reaction is expediently carried out at the reflux temperature of the solvent, and the two reactants can be added to the solvent simultaneously or successively. The alcohol can be removed by distillation from the mixture of solvent and alcohol R¹OH that is distilled out. The solvent can then be returned to the reaction. This variant can take place continuously. Potassium hydroxide can be added in solid form or as aqueous solution. Expediently, an aqueous solution of potassium hydroxide is added to the compound of formula (II) at the boiling point of the solvent.

The conduct of the reaction is particularly simple if the alcohol R₁OH is miscible with water. It is then possible to separate the water-alcohol R₁OH mixture from the solvent by phase separation. From the energy standpoint it is practical to use the aqueous potassium hydroxide solution in as concentrated a form as possible, in order to keep the energy needed to evaporate the water low. However, in principle, a 10 to 50% solution can be used. The isolation of the desired product (I) can be done very easily by filtration, since the compounds (I) crystallize out when the reaction batch is cooled. It is also possible to accelerate the reaction by adding phase-transfer catalysts such as quaternary phosphonium or ammonium compounds.

The compounds of formula (I) are valuable intermediate products for the production of plant-protection agents; see, for example DE-OS 33 41 669 and DE-OS 26 33 159. Moreover,

the compounds of formula (I) can be used as collectors in flotation. With them it is possible to enrich zinc from lead-zinc ores.

The compounds of formula (II) are known from Z. Obshch. Khim. [Journal of General Chemistry] 25, p. 828 (1955) and can be prepared by methods known from the literature.

The invention is illustrated by the following examples.

Example A

Preparation of potassium O-methyl-N-butyl-phosphoramidothioate

4.75 g technical grade caustic potash (85%) was added to 14.2 g (0.072 mol) O,O-dimethyl-N-butyl-phosphorothioamidate, which was in a three-neck flask with internal thermometer, stirrer and ascending condenser. While stirring, the heterogeneous mixture was slowly heated to an internal temperature of 130°C. At this temperature, an exothermic reaction suddenly began, with the internal temperature rising to +160°C. The methanol that was distilled out condensed in the receiver. The solid residue had a melting point of 110-115°C.

Yield: 15 g (~95% of theory).

Example B

Preparation of potassium O-ethyl-N-isopropyl phosphoramidothioate

1 mol (211 g) O,O-diethyl-N-isopropyl phosphoramidothioate was added to 470 mL xylene in a two-liter, four-neck flask with ascending condenser, vapor barrier, phase-separation vessel, reflux apparatus (for the solvent) and dropping funnel, and the solution was heated to reflux. At reflux, a solution of 65.8 g caustic potash (technical grade, 85%) in 50 mL water was then slowly added by drops. After an induction period, the reaction began, and a mixture of water, ethanol and xylene was distilled out. The water-ethanol mixture was separated in the phase separator. After the end of the addition of the caustic potash solution, heating at reflux was continued until the boiling point of xylene was reached. After cooling, the precipitated salt was suctioned out and dried. The result was 220 g (~91.3% of theory) potassium O-ethyl-N-isopropyl phosphoramidothioate with melting point 183°C.

Example C

Preparation of potassium O-ethyl-isopropylamido phosphoramidothioate

25.7 g O,O-diethyl-N-isopropyl phosphoramidothioate at room temperature was heated to 130°C while stirring in a four-neck flask equipped with stirrer, thermometer, dropping funnel and distillation head. Then, 14.6 g of a 50% aqueous KOH solution was slowly added by drops. After an induction period, an ethanol-water mixture distilled out. After the end of the addition, the mixture was stirred for another hour at 130°C and the reaction mixture was then cooled to

110°C. It was mixed with 28.9 g water and cooled to room temperature. A 43% ethanol-free aqueous solution of potassium O-ethyl-N-isopropyl phosphoramidothioate was obtained. The content was determined in various ways, for example, by titration or determination of density or high-pressure liquid chromatography. The pure salt can also be obtained by distilling the water out.

The compounds listed in Table 1 can be prepared by analogy with the procedures described in Example A or B.

Table 1

① Verbindung Nr.	R ₁	R ₂	R ₃	Fp. °C ②
1	CH ₃	C ₄ H ₉	H	110–115
2	CH ₃	CH ₃	H	88–90
3	CH ₃	CH ₃	CH ₃	
4	CH ₃	C ₄ H ₉ (iso)	H	164–166
5	C ₂ H ₅	C ₃ H ₇ (iso)	H	183
6	C ₂ H ₅	CH ₃	H	93–96
7	C ₂ H ₅	CH ₃	CH ₃	165–170
8	C ₂ H ₅	C ₂ H ₅	H	139–142
9	C ₂ H ₅	C ₄ H ₉	H	188–190
10	C ₂ H ₅	C ₁₂ H ₂₅	H	wachsig ③
11	C ₂ H ₅	C ₃ H ₇	H	168–170
12	C ₂ H ₅	C ₄ H ₉ (iso)	H	172–176
13	C ₂ H ₅	C ₂ H ₅	C ₂ H ₅	163–165
14	CH ₃	C ₃ H ₇	H	130–132
15	C ₄ H ₉	C ₄ H ₉ (tert.)	H	

Key	1	Compound No.
	2	M.p., °C
	3	Wax-like